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(54) Middle distillate compositions with improved cold flow properties.

(57) The low temperature properties of a distillate petroleum  
fuel oil boiling in the range 120°C to 500°C, and whose 20%  
and 90% distillation points differ by less than 100°C, and/or  
whose Final Boiling Point is in the range 340°C to 370°C are  
improved by the addition of a polymer or copolymer having at  
least 25 wt. % of n-alkyl groups of average number of carbon  
atoms from 12 to 14 with no more than 10 wt. % containing  
more than 14 carbon atoms.

**EP 0 153 176 A2**

Middle Distillate Compositions with Improved Cold Flow  
Properties

- 1 Mineral oils containing paraffin wax have the characteristic  
of becoming less fluid as the temperature of the oil  
decreases. This loss of fluidity is due to the  
crystallization of the wax into plate-like crystals which  
5 eventually form a spongy mass entrapping the oil therein.

It has long been known that various additives act as wax  
crystal modifiers when blended with waxy mineral oils.  
These compositions modify the size and shape of wax crystals  
and reduce the adhesive forces between the crystals and  
10 between the wax and the oil in such a manner as to permit  
the oil to remain fluid at a lower temperature.

- Various pour point depressants have been described in the  
literature and several of these are in commercial use. For  
example, U.S. Pat. No. 3,048,479 teaches the use of  
15 copolymers of ethylene and C<sub>3</sub>-C<sub>5</sub> vinyl esters, e.g.  
vinyl acetate, as pour depressants for fuels, specifically  
heating oils, diesel and jet fuels. Hydrocarbon polymeric  
pour depressants based on ethylene and higher alpha-olefins,  
e.g. propylene, are also known. U.S. Patent 3,961,916  
20 teaches the use of a mixture of copolymers, one of which is  
a wax crystal nucleator and the other a growth arrestor to  
control the size of the wax crystals.

- United Kingdom Patent 1263152 suggests that the  
size of the wax crystals may be controlled by using a  
25 copolymer having a lower degree of side chain branching.

1 It has also been proposed in for example United Kingdom Patent  
1469016 that the copolymers of di-n-alkyl fumarates and  
vinyl acetate which have previously been used as pour  
depressants for lubricating oils may be used as co-additives  
5 with ethylene/vinyl acetate copolymers in the treatment of  
distillate fuels with high final boiling points to improve  
their low temperature flow properties. According to United  
Kingdom Patent 1469016 these polymers may be C<sub>6</sub> to C<sub>18</sub>  
alkyl esters of unsaturated C<sub>4</sub> to C<sub>8</sub> dicarboxylic acids  
10 particularly lauryl fumarate and lauryl-hexadecyl fumarate.  
Typically the materials used are mixed esters with an  
average of about 12 carbon atoms (Polymer A). It is notable  
that the additives are shown not to be effective in the  
"conventional" fuels of lower Final Boiling Point (Fuels III  
15 and IV).

United States Patent 3252771 relates to the use of polymers  
of C<sub>16</sub> to C<sub>18</sub> alpha-olefines obtained by polymerising olefin  
mixtures that predominate in normal C<sub>16</sub> to C<sub>18</sub>  
alpha-olefines with aluminium trichloride/alkyl halide  
20 catalysts as pour point and cloud point depressants in  
distillate fuels of the broad boiling, easy to treat types  
available in the United States in the early 1960's.

With the increasing diversity in distillate fuels, types of  
fuel have emerged which cannot be treated by the existing  
25 additives or which require an uneconomically high level of  
additive to achieve the necessary reduction in their pour  
point and control of wax crystal size for low temperature  
filterability to allow them to be used commercially. One  
particular group of fuels that present such problems are  
30 those which have a relatively narrow, and/or low boiling  
range. Fuels are frequently characterised by their Initial  
Boiling Point, Final Boiling Point and the interim  
temperatures at which certain volume percentages of the

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nt  
a.

1 initial fuel have been distilled. Fuels whose 20% to 90%  
distillation point differ within the range of from 70 to  
100°C and/or whose 90% boiling temperature is  
5 from 10 to 25°C of the final boiling point and/or whose  
final boiling points are between 340 and 370°C have been  
found particularly difficult to treat sometimes being  
virtually unaffected by additives or otherwise requiring  
very high levels of additive. All distillations referred to  
herein are according to ASTM D86.

10 With the increase in the cost of crude oil, it has also  
become important for a refiner to increase his production of  
distillate fuels and to optimise his operations using what  
is known as sharp fractionation again resulting in distil-  
late fuels that are difficult to treat with conventional  
15 additives or that require a treat level that is unacceptably  
high from the economic standpoint. Typical sharply fract-  
tionated fuels have a 90% to final boiling point range of  
10 to 25°C usually with a 20 to 90% boiling range of less  
than 100°C, generally 50 to 100°C. Both types of fuel have  
20 final boiling points above 340°C generally a final boiling  
point in the range 340°C to 370°C especially 340°C to 365°C.

The copolymers of ethylene and vinyl acetate which have  
found widespread use for improving the flow of the  
previously widely available distillate fuels have not been  
25 found to be effective in the treatment of the narrow boiling  
and/or sharply fractionated fuels described above.  
Furthermore use of mixtures as illustrated in United Kingdom  
Patent 1469016 have not been found effective.

We have found however that polymers and copolymers  
30 containing very specific alkyl groups, such as specific  
di-n-alkyl fumarate/vinyl acetate copolymers, are effective  
in both lowering the pour point of the difficult to treat

- 1 fuels described above and controlling the size of the wax  
crystals to allow filterability including those fuels  
of the lower final boiling point in which the additives of  
United Kingdom Patent 1469016 were ineffective.
- 5 Specifically we have found that the average number of carbon  
atoms in the alkyl groups in the polymer or copolymer must  
be from 12 to 14 and that no more than 10 wt.% of the alkyl  
groups should contain more than 14 carbon atoms and  
preferably no more than 20 wt.% of the alkyl groups contain  
10 fewer than 12 carbon atoms. These polymers are particularly  
effective when used in combination with other low  
temperature flow improvers which on their own are  
ineffective in these types of fuels.

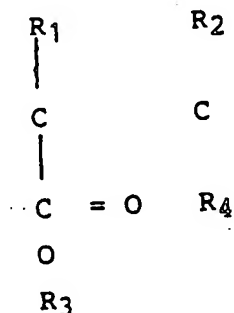
- The present invention therefore provides the use for  
15 improving the flow properties of a distillate petroleum fuel  
oil boiling in the range 120°C to 500°C, whose 20% and 90%  
distillation points differ by less than 100°C, and/or for  
improving the flow properties of a distillate fuel whose 90%  
to final boiling point range is 10 to 25°C and/or whose  
20 Final Boiling Point is in the range 340°C to 370°C of an  
additive comprising a polymer containing at least 25 wt.% of  
n-alkyl groups, the average number of carbon atoms in the  
n-alkyl groups is from 12 to 14 and no more than 10 wt.% of  
the alkyl groups contain more than 14 carbon atoms and  
25 preferably no more than 20 wt.% of the alkyl groups contain  
fewer than 12 carbon atoms.

- The additives are preferably used in an amount from 0.0001  
30 to 0.5 wt.%, preferably 0.001 and 0.2 wt.% based on the  
weight of the distillation petroleum fuel oil, and the  
present invention also includes such treated distillate  
fuel.

- 1 The preferred polymer is a copolymer containing at least 25 preferably at least 50 wt.% more preferably from 75 to 90 wt.% of a di-n alkyl ester of a dicarboxylic acid containing alkyl groups containing an average of 12 to 14 carbon atoms and 10 to 50 wt.% of another unsaturated ester such as a vinyl ester and/or an alkyl acrylate, methacrylate or alpha olefine. Equimolar copolymers of a di-n-alkyl fumarate and vinyl acetate are particularly preferred.

- 10 The polymers or copolymers used in the present invention preferably have a number average molecular weight in the range of 1000 to 100,000, preferably 1,000 to 30,000 as measured, for example, by Vapor Pressure Osmometry.

- 15 The carboxylic acid esters useful for preparing the preferred polymer can be represented by the general formula:



- 20 where in  $R_1$  and  $R_2$  are hydrogen or a  $C_1$  to  $C_4$  alkyl group, e.g., methyl,  $R_3$  is the  $C_{12}$  to  $C_{14}$  average, straight chain alkyl group, and  $R_4$  is  $COOR_3$ , hydrogen or a  $C_1$  to  $C_4$  alkyl group, preferably  $COOR_3$ . These may be prepared by esterifying the particular mono- or
- 25 di-carboxylic acid with the appropriate alcohol or mixture of alcohols.

- 1 Other unsaturated esters, which can be copolymerized are the C<sub>12</sub>-C<sub>14</sub> alkyl acrylates and methacrylates.

- 5 The dicarboxylic acid mono or di- ester monomers may be copolymerized with various amounts, e.g, 5 to 70 mole %, of other unsaturated esters or olefins. Such other esters include short chain alkyl esters having the formula:



- 10 where R' is hydrogen or a C<sub>1</sub> to C<sub>4</sub> alkyl group, R'' is -COOR''' or -OOCR''' where R''' is a C<sub>1</sub> to C<sub>5</sub> alkyl group branched or unbranched, and R''' is R'' or hydrogen. Examples of these short chain esters are methacrylates, acrylates, the vinyl esters such as vinyl acetate and vinyl propionate  
15 being preferred. More specific examples include methyl methacrylate, isopropenyl acetate and butyl and isobutyl acrylate.

- Our preferred copolymers contain from 40 to 60 mole % of a C<sub>12</sub>-C<sub>14</sub> average dialkyl fumarate and 60 to 40 mole % of  
20 vinyl acetate.

- Where ester polymers or copolymers are used they may conveniently be prepared by polymerising the ester monomers in a solution of a hydrocarbon solvent such as heptane, benzene, cyclohexane, or white oil, at a temperature  
25 generally in the range of from 20°C to 150°C and usually promoted with a peroxide or azo type catalyst, such as benzoyl peroxide or azodi-isobutyronitrile, under a blanket of an inert gas such as nitrogen or carbon dioxide, in order to exclude oxygen.



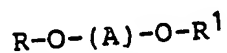
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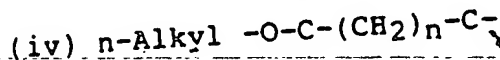
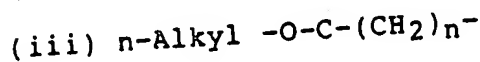
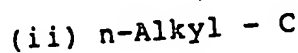
- 1 The additives of the present invention are particularly  
 effective when used in combination with other additives  
 known for improving the cold flow properties  
 of distillate fuels generally, although they may be used on  
 5 their own to impart a combination of improvements to the  
 cold flow behaviour of the fuel.

- The additives of the present invention are particularly  
 effective when used with the polyoxyalkylene esters, ethers,  
 ester/ethers and mixtures thereof, particularly those  
 10 containing at least one, preferably at least two C<sub>10</sub> to C<sub>30</sub>  
 linear saturated alkyl groups and a polyoxyalkylene glycol  
 group of molecular weight 100 to 5,000 preferably 200 to  
 5,000, the alkyl group in said polyoxyalkylene glycol  
 containing from 1 to 4 carbon atoms. These materials form  
 15 the subject of European Patent Publication 0061895 A2.

The preferred esters, ethers or ester/ethers useful in the  
 present invention may be structurally depicted by the  
 formula:



- 20 where R and R<sup>1</sup> are the same or different and may be  
 (i) n-Alkyl



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1 the alkyl group being linear and saturated and containing 10  
to 30 carbon atoms, and A represents the polyoxyalkylene  
segment of the glycol in which the alkylene group has 1 to 4  
carbon atoms, such as a polyoxymethylene, polyoxyethylene or  
5 polyoxytrimethylene moiety which is substantially linear;  
some degree of branching with lower alkyl side chains (such  
as in polyoxypropylene glycol) may be tolerated but it is  
preferred the glycol should be substantially linear.

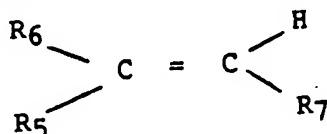
Suitable glycols generally are the substantially linear  
10 polyethylene glycols (PEG) and polypropylene glycols (PPG)  
having a molecular weight of about 100 to 5,000 preferably  
about 200 to 2,000. Esters are preferred and fatty acids  
containing from 10-30 carbon atoms are useful for reacting  
with the glycols to form the ester additives and it is  
15 preferred to use a C<sub>18</sub>-C<sub>24</sub> fatty acid, especially  
behenic acids, the esters may also be prepared by  
esterifying polyethoxylated fatty acids or polyethoxylated  
alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and  
20 mixtures thereof are suitable as additives with diesters  
preferred for use in narrow boiling distillates whilst minor  
amounts of monoethers and monoesters may also be present and  
are often formed in the manufacturing process. It is  
25 important for additive performance that a major amount of  
the dialkyl compound is present. In particular stearic or  
behenic diesters of polyethylene glycol, polypropylene  
glycol or polyethylene/polypropylene glycol mixtures are  
30 preferred.

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- 1 The additives of this invention may also be used with the ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers which may be copolymerized with ethylene, include unsaturated mono and diesters of the general formula:
- 5



- 10 wherein R<sub>6</sub> is hydrogen or methyl; a R<sub>5</sub> is a -OOCR<sub>8</sub> group wherein R<sub>8</sub> is hydrogen or a C<sub>1</sub> to C<sub>28</sub>, more usually C<sub>1</sub> to C<sub>17</sub>, and preferably a C<sub>1</sub> to C<sub>8</sub>, straight or branched chain alkyl group; or R<sub>5</sub> is a -COOR<sub>8</sub> group wherein R<sub>8</sub> is as previously described but is not hydrogen and R<sub>7</sub> is hydrogen or -COOR<sub>8</sub> as previously defined. The monomer, when R<sub>5</sub> and
- 15 R<sub>7</sub> are hydrogen and R<sub>6</sub> is -OOCR<sub>8</sub>, includes vinyl alcohol esters of C<sub>1</sub> to C<sub>29</sub>, more usually C<sub>1</sub> to C<sub>18</sub>, monocarboxylic acid, and preferably C<sub>2</sub> to C<sub>5</sub> monocarboxylic acid. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. We prefer
- 20 that the copolymers contain from 20 to 40 wt.% of the vinyl ester more preferably from 25 to 35 wt.% vinyl ester. They may also be mixtures of two copolymers such as those described in United States Patent 3961916.

- 25 It is preferred that these copolymers have a number average molecular weight as measured by vapor phase osmometry of 1000 to 6000, preferably 1000 to 3000,

- The additives of the present invention may also be used in distillate fuels in combination with polar compounds, either
- 30 ionic or nonionic, which have the capability in fuels of acting as wax crystal growth inhibitors. Polar nitrogen containing compounds have been found to be especially

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1 effective when used in combination with the glycol esters,  
ethers or ester/ethers and such three component mixtures are  
within the scope of the present invention. These polar  
compounds are generally amine salts and/or amides formed by  
5 reaction of at least one molar proportion of hydrocarbyl  
substituted amines with a molar proportion of hydrocarbyl  
acid having 1 to 4 carboxylic acid groups or their  
anhydrides; ester/amides may also be used contain 30 to 300  
preferably 50 to 150 total carbon atoms. These nitrogen  
10 compounds are described in U.S. Patent 4,211,534. Suitable  
amines are usually long chain C<sub>12</sub>-C<sub>40</sub> primary, secondary,  
tertiary or quarternary amines or mixtures thereof but  
shorter chain amines may be used provided the resulting  
nitrogen compound is oil soluble and therefore normally  
15 containing about 30 to 300 total carbon atoms. The nitrogen  
compound preferably contains at least one straight chain  
C<sub>8</sub>-C<sub>40</sub> preferably C<sub>14</sub> to C<sub>24</sub> alkyl segment.

Suitable amines include primary, secondary, tertiary or  
quaternary, but preferably are secondary. Tertiary and  
20 quarternary amines can only form amine salts. Examples of  
amines include tetradecyl amine, cocoamine, hydrogenated  
tallow amine and the like. Examples of secondary amines  
include dioctadecyl amine, methyl-behenyl amine and the  
like. Amine mixtures are also suitable and many amines  
25 derived from natural materials are mixtures. The preferred  
amine is a secondary hydrogenated tallow amine of the  
formula HNR<sub>1</sub>R<sub>2</sub> wherein R<sub>1</sub> and R<sub>2</sub> are alkyl groups  
derived from hydrogenated tallow fat composed of,  
approximately 4% C<sub>14</sub>, 31% C<sub>16</sub>, 59% C<sub>18</sub>.

30 Examples of suitable carboxylic acids for preparing these  
nitrogen compounds (and their anhydrides) include  
cyclo-hexane 1,2 dicarboxylic acid, cyclohexene dicarboxylic  
acid, cyclopentane 1,2 dicarboxylic acid, naphthalene

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- 1 dicarboxylic acid and the like. Generally these acids will have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene
- 5 dicarboxylic acids such as ortho-phthalic acid, para-phthalic acid, and meta-phthalic acid. Ortho-phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of di-hydrogenated tallow amine.
- 10 Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

- The relative proportions of additives used in the mixtures are from 0.5 to 20 parts by weight of the polymer of the invention containing the n-alkyl groups containing an
- 15 average of 12 to 14 carbon atoms to 1 part of the other additives such as the polyoxyalkylene esters, ether or ester/ether, more preferably from 1.5 to 9 parts by weight of the polymer of the invention.

- The additive systems of the present invention may
- 20 conveniently be supplied as concentrates for incorporation into the bulk distillate fuel. These concentrates may also contain other additives as required. These concentrates preferably contain from 3 to 75 wt.%, more preferably 3 to 60 wt.%, most preferably 10 to 50 wt.% of the additives
- 25 preferably in solution in oil. Such concentrates are also within the scope of the present invention:

- The present invention is illustrated by the following Examples in which the effectiveness of the additives of the present invention as pour point depressants and
- 30 filterability improvers were compared with other similar additives in the following tests.

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1 By one method, the response of the oil to the additives was  
measured by the Cold Filter Plugging Point Test (CFPP)  
which is carried out by the procedure described in detail  
in "Journal of the Institute of Petroleum", Volume 52,  
Number 510, June 1966, pp. 173-185. This test is designed  
5 to correlate with the cold flow of a middle distillate in  
automotive diesels.

In brief, a 40 ml sample of the oil to be tested is cooled  
in a bath which is maintained at about  $-34^{\circ}\text{C}$  to give  
non-linear cooling at about  $1^{\circ}\text{C}/\text{min}$ . Periodically (at each  
10 one degree Centigrade drop in temperature starting from at  
least  $2^{\circ}\text{C}$  above the cloud point) the cooled oil is tested  
for its ability to flow through a fine screen in a  
prescribed time period using a test device which is a  
pipette to whose lower end is attached an inverted funnel  
15 which is positioned below the surface of the oil to be  
tested. Stretched across the mouth of the funnel is a 350  
mesh screen having an area defined by a 12 millimetre  
diameter. The periodic tests are each initiated by applying  
a vacuum to the upper end of the pipette whereby oil is  
20 drawn through the screen up into the pipette to a mark  
indicating 20 ml of oil. After each successful passage the  
oil is returned immediately to the CFPP tube. The test is  
repeated with each one degree drop in temperature until the  
oil fails to fill the pipette within 60 seconds. This  
25 temperature is reported as the CFPP temperature. The  
difference between the CFPP of an additive free fuel and of  
the same fuel containing additive is reported as the CFPP  
depression by the additive. A more effective flow  
improver gives a greater CFPP depression at the same  
30 concentration of additive.

1 Another determination of flow improver effectiveness is  
made under conditions of the flow improver distillate  
operability test (DOT test) which is a slow cooling test  
5 designed to correlate with the pumping of a stored heating  
oil. In this test the cold flow properties of the described  
fuels containing the additives were determined by the DOT  
test as follows. 300 ml of fuel are cooled linearly at  
1°C/hour to the test temperature and the temperature then  
held constant. After 2 hours at the test temperature,  
10 approximately 20 ml of the surface layer is removed as the  
abnormally large wax crystals which tend to form on the  
oil/air interface during cooling. Wax which has settled in  
the bottle is dispersed by gentle stirring, then a CFPP  
filter assembly is inserted. The tap is opened to apply a  
15 vacuum of 500 mm of mercury, and closed when 200 ml of fuel  
have passed through 1 the filter into the graduated  
receiver. A PASS is recorded if the 200 ml are collected  
within ten seconds through a given mesh size or a FAIL if  
the flow rate is too slow indicating that the filter has  
20 become blocked.

CFPP filter assemblies with filter screens of 20, 30, 40,  
60, 80, 100, 120, 150, 200, 250 and 350 mesh number are  
used to determine the finest mesh (largest mesh number) the  
fuel will pass. The larger the mesh number that a wax  
25 containing fuel will pass, the smaller are the wax crystals  
and the greater the effectiveness of the additive flow  
improver. It should be noted that no two fuels will give  
exactly the same test results at the same treatment level  
for the same flow improver additive.

30 The Pour Point was determined by two methods, either the  
ASTM D 97 or a visual method in which 100 ml samples of fuel  
in a 150 ml narrow necked bottle containing the additive  
under test, are cooled at 1°C/hour from 5°C above the wax

- 1 appearance temperature. The fuel samples were examined at  
3°C intervals for their ability to pour when tilted or  
inverted. A fluid sample (designated F) would move readily  
on tilting, a semi-fluid (designated semi-F) sample may need  
5 to be almost inverted, while a solid sample (designated S)  
can be inverted with no movement of the sample.

The fuels used in these Examples were:

ASTM-D-86 Distillation, °C					
Fuel	Wax	Initial	20%	90%	Final
	Appearance Point	Boiling Point			Boiling Point
10	A	-5	202	270	328
	B	-2	202	254	340
	C	-2.5	274	286	330
	D	-4	155	215	335
	E	-1.5	196	236	344
15					

The Additives used were as follows:

Additive 1: A polyethylene glycol of 400 average  
molecular weight esterified with 2 moles of behenic acid.

- 20 Additive 2: A copolymer of a mixed C<sub>12</sub>/C<sub>14</sub> alkyl fumarate  
obtained by reaction of 50:50 weight mixture of normal C<sub>12</sub>  
and C<sub>14</sub> alcohols with fumaric acid and vinyl acetate  
prepared by solution copolymerisation of a 1 to 1 mole ratio  
mixture at 60°C using azo diisobutyronitrile as catalyst.



1 The results in the CFPP and Pour Point tests were as follows:  
ASTM D 97

Fuel	Additive	Amount ppm	CFPP	CFPP Depression	Pour Point
5	A	None	-5°C		-9°C
		1	-8°C	3°C	-6°C
		2	-3°C	-2°C	-15°C
		2:1	-9°C	4°C	-18°C
		2:1	-11°C	6°C	-18°C
		300:200			
10	B	None	-4°C		-6°C
		1	-8°C	4°C	-6°C
		1			-15°C
		2	-2°C	-2°C	
		2	-11°C	7	-18°C
		2:1	-13°C	9	-21°C
15	C	None	-4°C		-6°C
		1	-8°C	4	-3°C
		1	-7°C	3	
		2	-2°C	-2	
		2:1	-6°C	2	-12°C
		2:1	-10°C	6	-15°C
20		1000			
		1000			
		300/200			
		600/400			

25 The additives of the invention were compared in the DOT test  
with Additive 3 which was an oil solution containing 63 wt. %  
of a combination of polymers comprising 13 parts by weight  
of an ethylene/vinyl acetate copolymer of number average  
molecular weight 2500 and vinyl acetate content of 36 wt. %  
and 1 part by weight of a copolymer of ethylene and vinyl  
30 acetate of number average molecular weight 3500 and a vinyl  
acetate content of about 13 wt. %.

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DOT Test

ppm of additive to pass DOT (120 mesh) at -10°C

Fuel	Additive 3		Mixture of 3 Parts of 1 and 2 Parts of 2	
5	A	>3,000	700	
	B	800	250	
	C	1,500	700	
	D	1,250	500	
	E	>1,500	300	

Various fumarate/vinyl acetate copolymers were tested in admixture (3 parts) with Additive 1 (2 parts) to determine the effect of the chain length in the fumarate with the following results.

	Fuel	Alcohols used to make fumarate	Average C Number in fumarate	Pour Point Test Appearance at -10°C	CFPP Depression 500 ppm(ai)	1,000 ppm (ai)
15	A	C-8	8	S	2	3
		C-9	9	-	2	-
		C-10	10	S	3	3
20		C-10/C-12	11	S	3	4
		C-11	11	-	3	3
		C-12	12	S	3	4
		C-12/C-14	13	F	5	7
		C-14	14	F	-2	-2

1	Fuel	Alcohols used to make fumarate	Average C Number in fumarate	Pour Point Test Appearance at -10°C	CFPP Depression 300 ppm
	B				
		C-8	8	S	3
5		C-9	9	-	5
		C-10	10	S	4
		C-10/C-12	11	S	5
		C-11	11	-	5
		C-12	12	S	3
10		C-12/C-14	13	F	7
		C-14	14	F	0

				1,000 ppm
				3
15	C	C-10	10	3
		C-10/C-12	11	3
		C-11	11	3
		C-12	12	6
		C-12/C-14	13	0
		C-14	14	3
20		C-18	18	

25 Various fumarate/vinyl acetate copolymers, obtained from different alcohols but averaging 12 to 13.5 carbon atoms in the alkyl groups were tested in the same mixture as in the previous example in the CFPP and Visual pour point tests with the following results.

Fumarate Alcohols  
(All n-alcohols except oxo-C-13)  
Ratio's by weight

	Alcohol Average C-number	Fuel A			Fuel B			Fuel C		
		CFPP Depression		Pour Point	CFPP Depression	500	Pour Point	CFPP Depression	1000	Pour Point
		500 ppm	1000 ppm	Appearance at -10°C	300 ppm	500 ppm	Appearance at -10°C	300 ppm	500 ppm	Appearance at -10°C
Fumarate Alcohols										
(All n-alcohols except oxo-C-13)										
ratio's by weight										
1.	C-12/C-14 = 1/1	13.0	5	7	F	7	9	F	6	F
2.	C-12/C-14 = 3/1	12.5	2	4	Semi-F	6	6	Semi-F	3	-
3.	C-12/C-14 = 1/3	13.5	0	1	F	2	5	F	0	-
4.	C-10/C-16 = 1/1	13.0	-2	-1	F	2	1	F	1	-
5.	C-13 oxo (from tetrapropylene)	13.0	3	-	S	5	5	S	3	-
6.	C-12/C-14/C-16 = 2/1/1	13.5	1	-	-	1	-	-	0	-
7.	C-12/C-14/C-16 = 8/3/1	12.7	4	7	F	7	9	F	7	F
8.	C-8/C-10/C-12/C-14/C-16/C-18 = 9/11/36/30/10/4	12.2	4	6	F	4	7	F	2	F
9.	Ditto = 3/8/33/37/12/8	13.0	0	1	-	2	2	-	1	-
10	C-12/C-14/C-16/C-18 = 45/38/12/5	13.4	0	0	-	2	2	-	1	-
11.	C-8 to C-18 = 13/10/41/15/9/13	12.5	2	3	-	4	6	-	1	-

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A

- 1 The fuels B and C were used in the following Examples together with

Fuel F	ASTM D-86 Distillation °C				FBP
	IBP	20%	50%	90%	
5	182	254	285	324	343

- 10 The results are CFPP and visual Pour Point results shown for various additives in the following table. Where the additive has no pour depressing effect the CFPP value is not measured because without pour depression the fuel cannot be used.

Fuel BCFPP Depression

Additive	400 ppm Fumarate vinyl acetate Additive 1	400 ppm fumarate/vinyl acetate 100 ppm Additive 1 100 ppm Additive 3
Alcohol content of Fumarate	100 ppm	
C <sub>4</sub> )		2
C <sub>6</sub> )		2
C <sub>8</sub> )		2
C <sub>9</sub> )	No pour depression*	2
C <sub>10</sub> )		2
C <sub>11</sub> )		2
C <sub>12</sub> )		8
C <sub>13</sub> )	- 7°C	2
C <sub>14</sub> )	0	Raised by 2°C
C <sub>16</sub> )	Raised by 2°C	
C <sub>18</sub> )	No pour depression*	
C <sub>22</sub> )		
Mixed C <sub>12</sub> /C <sub>14</sub>		
3:1	No effect	2
1:1	8°C	9
1:3	4°C	5
C <sub>18</sub> /C <sub>16</sub>		
1:1	Raised by 1°C	Raised by 1°C
C <sub>10</sub> /C <sub>12</sub>	No effect	2

\* No pour depression observed at -10°C after the 1°C/hour cool.

CFPP Depression

Additive	<u>Fuel C</u>		<u>Fuel F</u>	
	800 ppm F/VA 200 ppm Additive 1	800 ppm F/VA 200 ppm Additive 1	800 ppm F/VA 200 ppm 1 100 ppm 3	
Alcohol content of Fumarate				
C <sub>4</sub> )				
C <sub>6</sub> )				
C <sub>8</sub> )				
C <sub>9</sub> )				
C <sub>10</sub> )				
C <sub>11</sub> )				
C <sub>12</sub> )	3	9	4	
C <sub>13</sub> )	0	1	1	
C <sub>14</sub> )	0	2	-	
C <sub>16</sub> )				
C <sub>18</sub> )				
C <sub>22</sub> )				
Mixed C <sub>12</sub> /C <sub>14</sub>				
3:1				1
1:1				8
1:3				4
C <sub>18</sub> /C <sub>16</sub>				
1:1				
C <sub>10</sub> /C <sub>12</sub>				
1:1				

No pour depression\*

No pour depression\*

No pour depression\*

No pour depression\*

\*No pour depression observed at -10°C after the 1 hour cool

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- 1 The Additives were also tested in combination with Additive 4 the half amide formed by reacting two moles of hydrogenated tallow amine with phthalic anhydride and the CFPP depressions in Fuel B were as follows

5	Additive	CFPP Depressions
	Additive 4 (250 ppm)	6
	Additive 3 (100 ppm)	
	C <sub>12</sub> /C <sub>14</sub> F/VA (250 ppm)	
10	Additive 4 (300 ppm)	
	Additive 1 (100 ppm)	6
	C <sub>12</sub> E/C <sub>14</sub> F/VA (100 ppm)	
	Additive 4 (250 ppm)	0
	C <sub>12</sub> /C <sub>14</sub> F/VA (250 ppm)	



## 1 CLAIMS

- 1           The use for improving the low temperature  
properties of a distillate petroleum fuel oil boiling in the  
range 120°C to 500°C, and whose 20% and 90% distillation  
5   points differ by less than 100°C, and/or whose 90% to  
final boiling point range is 10 to 25°C and/or whose Final  
Boiling Point is in the range 340°C to 370°C of an additive  
comprising a polymer or copolymer containing at least 25  
wt.% of n-alkyl groups wherein the average number of carbon  
10   atoms in the n-alkyl groups is from 12 to 14 and no more  
than 10 wt.% of alkyl groups containing more than 14 carbon  
atoms.
- 2           A distillate petroleum fuel oil according to claim  
1 in which no more than 20 wt.% of the alkyl group  
15   contains fewer than 12 carbon atoms.
- 3           The use according to claim 1 or claim 2 in which the  
polymer is of a di-n-alkyl ester of a mono-ethylenically  
unsaturated C<sub>4</sub> to C<sub>8</sub> or dicarboxylic acid.
- 4           The use according to any of the preceding claims  
20   in which the copolymer is of a di-n alkyl ester of  
dicarboxylic acid in which the alkyl groups containing an  
average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a  
vinyl ester, an alkyl acrylate or methacrylate.

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1        5            The use according to any of the preceding claims  
as a co-additive with a polyoxyalkylene ester, ether,  
ester/ether and mixtures thereof, containing at least two  
C<sub>10</sub> to C<sub>30</sub> linear saturated alkyl groups and a  
5 polyoxyalkylene glycol of molecular weight 100 to 5,000  
preferably 200 to 5,000, the alkyl group in said  
polyoxylakylene glycol containing from 1 to 4 carbon atoms.

6            The use according to any of the preceding claims  
in combination with polar compounds, either ionic or  
10 nonionic, which have the capability in fuels of acting as  
wax crystal growth inhibitors.

7            The use according to Claim 6 in which the polar  
compounds are the amine salts and/or amides formed by  
reaction of at least one molar proportion of  
15 hydrocarbyl-substituted amines with a molar proportion of  
hydrocarbyl acid having 1 to 4 carboxylic acid groups or  
their anhydrides containing a total of 30 to 300 carbon  
atoms.

8            A distillate petroleum fuel oil boiling in the  
20 range 120°C to 500°C and whose 20% and 90% distillation  
points differ by less than 100°C, and/or whose 90% to final  
boiling point is 10 to 25°C and/or whose Final Boiling Point  
is in the range 340°C to 370°C. containing from 0.001 to 0.5  
wt.% of a polymer or copolymer containing at least 25 wt.%  
25 of n-alkyl groups wherein the average number of carbon atoms  
in the n-alkyl groups is from 12 to 14, there being present  
no more than 10 wt.% of alkyl groups containing more than 14  
carbon 25 atoms.

0  
1 9 A distillate petroleum fuel oil according to Claim  
8 in which the copolymer is of a di-n alkyl ester of a  
dicarboxylic acid in which the alkyl groups containing an  
average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a  
5 vinyl ester, alkyl acrylate or methacrylate.

10 A distillate petroleum fuel oil according to  
Claim 8 or Claim 9 containing as a co-additive a  
polyoxyalkylene ester, ether, ester/ether and mixtures  
thereof, containing at least two C<sub>10</sub> to C<sub>30</sub> linear  
10 saturated alkyl groups and a polyoxyalkylene glycol of  
molecular weight 100 to 5,000 preferably 200 to 5,000, the  
alkyl group in said polyoxyalkylene glycol containing from 1  
to 4 carbon atoms.

11 A distillate petroleum fuel oil according to Claim  
20 10 containing from 0.5 to 20 parts by weight of the ester  
copolymer per part of the polyoxyalkylene ester, ether or  
ester/ether.

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1 CLAIMS FOR AUSTRIA

1 A process for improving the low temperature  
properties of a distillate petroleum fuel oil boiling in the  
range 120°C to 500°C, and whose 20% and 90% distillation  
5 points differ by less than 100°C, and/or whose 90% to final  
boiling point range is 10 to 25°C and/or whose Final Boiling  
Point is in the range 340°C to 370°C comprising adding  
thereto a polymer or copolymer containing at least 25 wt.%  
of n-alkyl groups wherein the average number of carbon  
10 atoms in the n-alkyl groups is from 12 to 14 and no more  
than 10 wt.% of alkyl groups containing more than 14 carbon  
atoms.

2 A process according to claim 1 in which no more  
15 than 20 wt.% of the alkyl group contains fewer than 12  
carbon atoms.

3 A process according to claim 1 or claim 2 in which  
the polymer is of a di-n-alkyl ester of a mono-ethylenically  
unsaturated C<sub>4</sub> to C<sub>8</sub> or dicarboxylic acid.

4 A process according to any of the preceding claims  
20 in which the copolymer is of a di-n alkyl ester of  
dicarboxylic acid in which the alkyl groups containing an  
average of 12 to 14 carbon atoms and from 10 to 50 wt.% of a  
vinyl ester, an alkyl acrylate or methacrylate.

1 5 A process according to any of the preceding claims  
e as a co-additive with a polyoxyalkylene ester, ether,  
5 ester/ether and mixtures thereof, containing at least two  
C<sub>10</sub> to C<sub>30</sub> linear saturated alkyl groups and a  
polyoxyalkylene glycol of molecular weight 100 to 5,000  
preferably 200 to 5,000, the alkyl group in said  
polyoxylakylene glycol containing from 1 to 4 carbon atoms.

6 A process according to any of the preceding claims  
1 in combination with polar compounds, either ionic or  
10 nonionic, which have the capability in fuels of acting as  
wax crystal growth inhibitors.

7 A process according to Claim 6 in which the polar  
compounds are the amine salts and/or amides formed by  
reaction of at least one molar proportion of  
15 hydrocarbyl-substituted amines with a molar proportion of  
hydrocarbyl acid having 1 to 4 carboxylic acid groups or  
their anhydrides containing a total of 30 to 300 carbon  
atoms.

8 A process according to any of the preceding claims  
20 in which from 0.001 to 0.5 wt.% of the polymer or copolymer.  
is added.

**EUROPEAN PATENT APPLICATION**

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(54) Middle distillate compositions with improved cold flow properties.

(57) The low temperature properties of a distillate petroleum fuel oil boiling in the range 120°C to 500°C, and whose 20% and 90% distillation points differ by less than 100°C, and/or whose Final Boiling Point is in the range 340°C to 370°C are improved by the addition of a polymer or copolymer having at least 25 wt.% of n-alkyl groups of average number of carbon atoms from 12 to 14 with no more than 10 wt.% containing more than 14 carbon atoms.



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# EUROPEAN SEARCH REPORT

0153176

Application number

EP 85 30 1047

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-2 305 492 (EXXON) * Claims 1-3,7-10,12-14; page 7, line 7 - page 8, line 18; page 8, line 27 - page 9, line 18; page 13, lines 16-31; page 16, line 33 - page 17, line 18; page 18, lines 20-23; page 20, examples 7,12 *	1,2,8	C 10 L 1/18
X	FR-A-2 305 493 (EXXON) * Claims 1-3,7,9,10; page 7, line 7 - page 7, line 18; page 8, line 27 - page 9, line 18; page 13, lines 16-31; page 15, line 39 - page 16, line 18; page 17, lines 1-23; page 9, examples 5,9 *	1,2,8	
X	GB-A- 573 364 (STANDARD OIL DEV.) * Claims 1-3; page 1, lines 54-90 *	1,2,10	TECHNICAL FIELDS SEARCHED (Int. Cl.4) C 10 L
X	US-A-3 413 103 (D.W. YOUNG) * Claims 1,4-6; column 2, lines 8-35; column 2, line 50 - column 3, line 13 *	1-4,8,9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-08-1985	Examiner RO TSAERT L.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	



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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
D,X	GB-A-1 469 016 (EXXON)  * Claims 1,5,7,8; page 3, lines 1-53; page 4, lines 32-50; page 6, lines 44-55; page 7, lines 17-20 *	1-4,8,9	
D,A	--- US-A-4 211 534 (N. FELDMAN)  * Claims 1,3-6,13; column 4, line 46 - column 5, line 55; column 7, line 59 - column 9, line 65 *	1-4,8,9	
Y		6	
A	--- EP-A-0 061 894 (EXXON)  * Claims 1,5-10,11,13-14,17; page 21, example 17 *	1,6,7,8	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	--- EP-A-0 061 895 (EXXON)  * Claims 1-11,14,16-22 *	1,5-8,10,11	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-08-1985	Examiner RO TSAERT L.D.C.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	